Electrophoretic Deposition for Improved Trace Element Homogeneity in Silica Reference Materials

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Introduction and Motivation

The following steps summarize the experiment.
1. Generate feedstocks via the Stöber process.23
2. Consolidate samples using either EPD or DP.
3. Density by sintering in a reducing environment.
4. Mount in epoxy and polish flat for analysis.

While EPD is attractive for making fully custom reference materials, we aim in this work to further validate our method by analyzing two sets of new EPD samples. For a control, equivalent samples were compressed mechanically by die-pressing (DP).

Spatially resolved techniques such as laser ablation mass spectrometry can quantitatively characterize heterogeneity in spatial dopant distribution.

Sample Images and Description

Samples were fabricated from SiO2 nanoparticle feedstocks (Fig. 2, top images). The particles were doped with -1 ppm of over 40 trace elements from Li to U.

One EPD and one DP sample from each feedstock were analyzed. Set 1 uses partial additions of silica precursor (Fig. 3, L) while Set 2 uses one addition of the same total amount. Thus, EPD and DP can be intercompared with Set 1 and Set 2 (Fig. 4, R).

Experimental Methods

The following steps summarize the experiment.
1. Generate feedstocks via the Stöber process.
2. Consolidate samples using either EPD or DP.
3. Density by sintering in a reducing environment.
4. Mount in epoxy and polish flat for analysis.

Results

The lowest RSD (0.03) was observed for 141Pr in the Set 2 EPD sample, which exhibited RSD ≤ 0.10 for 29 of 39 elements. By contrast, the lowest Set 1 RSD was 0.21 (105Dy, 193Ho, 175Lu), also seen in EPD.

Only 4 analytes (112Ag, 115Cd, 119In, and 229Th) showed an RSD worse in EPD than in DP. The remaining 35 showed lower RSD in EPD samples.

Discussion

Generally, the dopant heterogeneity in both Sets 1 and 2 was greatly improved in EPD samples relative to DP. Although this result supports the hypothesis that EPD is driving this effect, the mechanism of action is not yet well understood.

The difference between Set 1 and Set 2 was also significant beyond the trend in observed EPD effects, with Set 2 generally favored. This outcome motivates the adoption of a synthesis like the one used for Set 2 in fabricating future samples.

Conclusions

A trend in improved homogeneity of spatial dopant distribution was observed in EPD samples versus DP, with observed RSD as low as 0.03. EPD shows potential as a new method of fabricating customizable glassy reference materials for use in method development and QC applications.

Confirmatory measurements are warranted using a compatible technique beyond LA-ICP-MS, such as secondary ion mass spectrometry (SIMS). Like LA-ICP-MS, SIMS is a spatially resolved technique which benefits from homogeneity in reference materials. Nanoscale SIMS imaging may be able to elucidate informative microstructural features.

Additional parameter space in the fabrication of this type of sample is open to exploration, in steps such as sintering and even the EPD process itself.

References and Acknowledgments

[5] LabDirect, LLC. ammonium/ammonium hydroxide
[8] Sigma-Aldrich, tetrahydroxyaluminate
[9] Vedantu.com, the correct electron dot structure of water

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